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Application of chitosan-silver nanocomposites for heavy metals removal: A Review Study

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Abstract

Increased releases of heavy metals into environment due to rise in both industrial and anthropogenic activities has result to serious destruction of water quality. This demands urgent need for treatment of wastewater of any form, so as to remove the pollutants. Sequestration of heavy metals from wastewater continue to be a huge challenge and enormous number of materials have been examined for their capacities in this case. However, the exploration still continues to uncover the most excellent material. As a substitute to common materials, nanocomposites of biopolymer such as chitosan appear to offer new prospect to deal with this challenge. Chitosan as a biopolymer has it sources to be non – toxic in nature and are found naturally in abundance as wastes. In this review, necessary information regarding recent studies on chitosan-silver nanocomposites and other chitosan nanocomposites used in removal of heavy metals and other pollutants from water/wastewater were discussed.

1. Introduction

A nanocomposite is defined as a blend of two or more materials in which at least one of the components is in nanosize **[1]**. These materials are usually of different physical properties, chemical properties and apparent interface **[2]**. Their numerous advantages over the individual component include higher toughness, higher stiffness, high specific strength, gas barrier characteristics, flame retardancy, corrosion, and resistance **[3, 4]**. Nanocomposites have diversified applications in areas such as biological sciences, drug delivery systems and wastewater treatment **[5]**. In nanocomposites, the nano-component is incorporated into functioned materials such as carbon nanotubes, activated carbon, reduced grapheme oxide and different polymeric matrices for numerous applications, which efficient handling of water pollutions is one **[6]**.

Water free of pollution is a natural resource that is extensively needed in all human endeavours. Without it, the most essential aspects of man’s life; health, food, energy, and economy is not safe **[7]**. Also, environmental, economic and social effects, and social effects of poor-quality water supply threaten the safety of children and the impoverished **[8]**. It is estimated that about twenty (20) millions of human lives are lost annually as a result of waterborne problems, while on a daily basis about six thousand infants lose their lives due to water-related problems **[9]**. Currently, about a billion of people living in the world are without access to safe water, which results in major health challenges. In addition to the problems of water pollution faced by man, there is limited access to available safe water due to competing demands of increasing further due to climate changes and geometric population growth in the next two decades [9].

Water pollution is caused by the presence pollutants and these pollutants are majorly grouped into health problem causing and ecosystem disruption pollutants as shown in **Table 1** [10]. Among the health problem causing pollutants are heavy metals [11]. Heavy metals are elements having atomic weights between 63.5 and 200.6 and specific gravities greater than 5.0 [12]. With the fast growth in human and industrial activities, wastewater pollute by heavy metals is directly or indirectly released into the environment in large volumes, particularly in developing countries [13]. Heavy metals are not biodegradable therefore have tendency to build up in living organisms to become toxic [14].

In recent years, heavy metal remediation of wastewater has been carried out on the using various nanocomposites as adsorbents [15]. These nanocomposites provide high surface areas and specific affinities for heavy metals adsorption from the aqueous systems [16]. Hence, the adsorption of heavy metal ions as pollutants from contaminated water using nanocomposites has attracted significant attention due to their characteristic's properties such as extremely small sizes, very large surface areas and high surface-area-to volume ratios. It has also been established that they have the better adsorption capacity, selectivity and stability than nanoparticles [17].

Therefore, nanocomposites have been considered helpful as agents in the removal of toxic substances contributing to the development of more efficient treatment processes among the highly developed water systems [18]. Currently, there are numerous nanomaterials used for the various problems of water pollution in order to ensure environmental stability. Hence, this review provides an exclusive insight on the basic use of nanocomposites for water/wastewater treatment and reuse while focussing on the challenges of future research. Thus, this review tried to look into the recent and updated published works regarding the preparation and application of chitosan-silver nanocomposite as agent for the removal of heavy metals and other pollutants.

Table 1: Common pollutants of water

SN	Health Problems causing pollutants	Sources	Ecosystem Disruption causing pollutants	Sources
1	Microorganisms. Such as bacteria, viruses, parasites	Human and animal wastes	Sediment such as soil and silts	Land erosion
2	Organic pollutants. Such as pesticides, plastics, detergents, oil, gasoline	Industrial, domestic, and agricultural	Plant nutrients such as nitrates and phosphates	Agricultural and urban fertilizers, sewage, manure
3	Inorganic pollutants such as heavy metals, salts	Industrial effluents, domestic cleansers, surface runoff	Oxygen-demanding wastes such as manure from animal and residues from plants	Sewage, agricultural runoff, paper mills, food processing
4	Radioactive pollutants such as uranium, thorium, caesium, iodine, radon	Mining and processing or ores, power plants, weapons production, natural sources	Thermal such heat	Power plants, industrial cooling

2. Sustainability of water using nano-biopolymeric material

The uses of synthetics materials for the removal of heavy metals from wastewater face some drawbacks caused by their high cost of development, toxic and non-biodegradable nature [15]. Hence, treatment of wastewater using efficient and low-cost adsorbents is always highly encouraged [19]. As a result of this, biopolymers in place of other adsorbents are suspected to possess some potential for wastewater treatment by adsorption [20]. Among the existing biopolymers, the one commonly used for wastewater treatment is chitosan but itself need some kind of improvements to boost it efficiency which is believed can be achieved using nanotechnology [21]. Hence, recently, so much interest in terms of improving existing biopolymer adsorbents using nanotechnology were shown by researchers [22]. Nanotechnology is an aspect of science that involves development of materials of sizes between 0 to 100 nm [23]. These materials are commonly referred to as nanomaterials; they exist in various forms (Figure 1) and have numerous applications, which wastewater treatment is one [23]. The uses of chitosan incorporated with nanoparticles of metal especially silver to form nanocomposite have been an area of interest of stakeholders in wastewater treatment [24]. Therefore, nanocomposites of chitosan will therefore add to the inventory of efficient and low-cost adsorbents.

Generally, nanocomposites of chitosan have distinctive properties which include availability of numerous active sites for binding of metal ions, large surface area, biodegradability and easy regeneration [25]. Several researches have been done using nanocomposites of biopolymer as nano-adsorbents in recent years [26-29]. The properties of these materials account for their high adsorption potentials in wastewater treatment [30]. The frequently used adsorbents for wastewater treatment include activated carbon, clay, biomaterials, silica, metal oxides and nanoparticles [31]. Among the listed common adsorbents, biomaterials which chitosan is one have gained the interest of researchers in wastewater remediation processes due to their cost-effectiveness and abundance of sources [32].

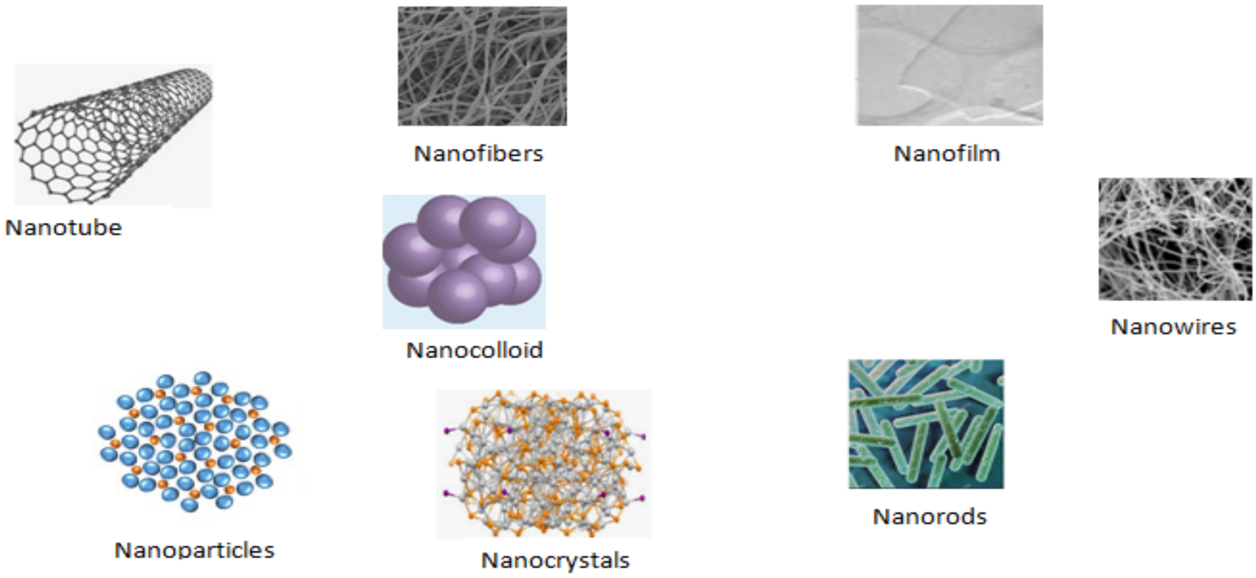

Figure 1: Images of some nanomaterials [33]

3. The need for chitosan as adsorbent

Chitosan is the second most abundant biopolymer after cellulose, which when undergone deacetylation produces chitosan. Chitosan formed part of structural component of sea shells such as crab, shrimp, shellfish, and krill. It can also be found in mollusks, insects, crustaceans, fungi and algae [34]. Naturally, chitosan compared to order adsorbents, is non-toxic, biodegradable, biocompatible, and antibacterial [35], this makes its stand out as the most appropriate choice for sequestration of adsorbates particularly heavy metal. It has also attracted considerable interest due to its antimicrobial and antifungal activities [36]. The action of chitosan is dependent on factors such as the source, the degree of deacetylation and some other physicochemical properties [37]. The chemical structure (Figure 2) of chitosan shows a randomly distributed β- (1-4)-linked D-glucosamine and N-acetyl-D-glucosamine components derived by deacetylation of chitin [38]. Three kinds of functional groups namely amino group, primary and secondary hydroxyl groups are present in chitosan [38]. The amine group allows the strong electrostatic interactions with other substances [39]. Chitosan exhibits chemical reaction usual of amines, of which N-acylation and Schiff reaction are the most common and important [40].

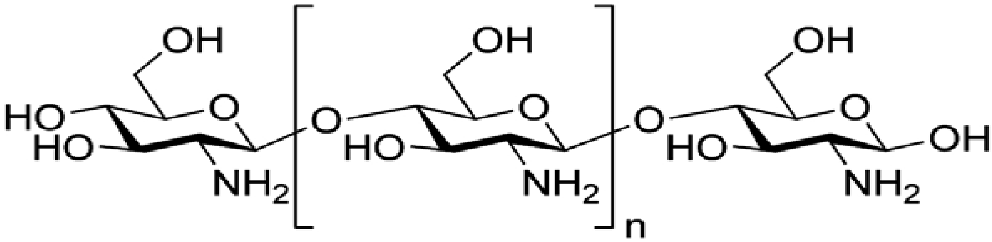

Figure 2: Chemical structure of chitosan [41]

Commercially, chitosan is commonly produced via chemical deacetylation of crustacean chitin using slight concentrated sodium hydroxide [42]. Chitosan obtained from crustacean chitosan is not consistent in its physicochemical properties as a result of different kinds of raw materials and extraction conditions [43]. The extraction of chitin from source like crab shells involves three main processes which include decalcification or demineralization (which is the removal of the minerals mainly calcium using dilute aqueous solution of HCl). This is followed by deproteinization involving the removal of protein content, peptides and caroteniod pigments as well as other lipids using dilute aqueous solution of NaOH with constant stirring and lastly deacetylation process (removal of acetyl groups from the chitin to obtain chitosan) [44]. The schematic diagram of process of chitosan preparation from crab shell is presented in **Figure 3**.

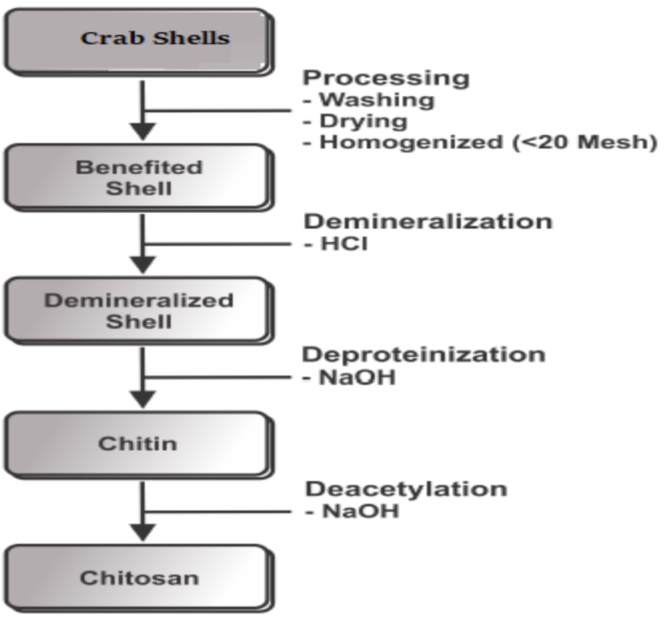

Figure 3: Schematic diagram of the preparation of chitosan from crab shells [45].

For some decades now, chitosan has been employed as an adsorbent to sequestrate heavy metals from wastewater due to the presence of numbers of amino and hydroxyl groups, which act as active binding sites [15]. This biopolymer stands for a likeable substitute to other biomaterials due to its physicochemical characteristics, high reactivity, outstanding chelation performance and high selectivity towards pollutants [46]. Globally, the solid waste from the processing of shellfish, krill, shrimps, and crabs make up large quantity of industrial waste from food industries [47]. This enormous waste can be converted to chitosan via dimerialization, deproteinization and partial deacetylation to produce a low-cost biodegradable adsorbent [48]. Chitosan, even though has high adsorption capacity for many heavy metals has shortcomings such as instability during applications and storage due to some factors which include weak mechanical property, and low density. These shortcomings can be overcome through modifications using numerous methods [49]. However, addition of stabilizing agents in the form of nanoparticles of metals like gold, copper, zinc and silver is so much believed to improve the physicochemical properties of chitosan due to high stability exhibits by silver metal [50].

4. Preparation of chitosan – silver nanocomposite

A number of methods have been used for the preparation of chitosan nanocomposites and were grouped into chemical, green, thermal, gamma ray irradiation, thermal, UV irradiation, and electrochemical methods [51]. Among these methods, green method (**Figure 4**) using plant extracts have been known to be the most excellent and these was well researched [52, 53]. The method is reported to be the easiest and the most cost-effective owing to the large abundance of plant rich in phytochemicals [54]. Though, there are still continuous researches on the preparation chitosan-metal nanocomposites using others method [55].

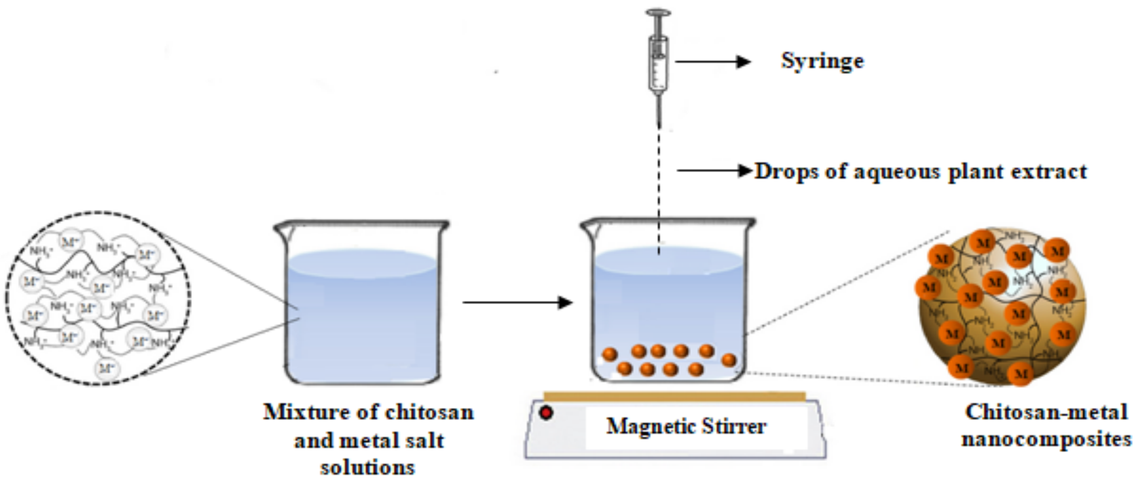

Figure 4: A schematic diagram of the green preparation of chitosan-metal nanocomposites [64].

In general, the green method primarily includes the use of chitosan solutions as the precursors [42, 56]. During the preparation, aqueous plant extract is place into a mixture of chitosan and metal salt solutions. The mixture is stir using a magnetic stirrer, allowed to age and change in colour is watched. The change in colour of the mixture signifies the formation of nanocomposite [57]. The plant extracts mostly act to reduce the metal ions in the solution to metal nanoparticles and at the same time stabilizes its. The metal nanoparticles formed diffuse into the chitosan polymer matrix while the excess spread across the surface [58]. After the formation of nanocomposites, sedimentation is allowed and sediment is freeze dried to obtain the nanocomposites [59].

The existence of numerous amine (–NH_2) and hydroxyl (–OH) groups in chitosan polymer chain boost its adsorption potential for metal ions. The groups (–NH_2 and –OH) are the binding sites for heavy metal ions [60]. Conversely, the major shortcomings of chitosan which affect its adsorption capabilities are instability at higher temperature, weak mechanical strength and low porosity [61]. These shortcomings can be overcome using either physical or chemical modifications which involves incorporation metal/metal oxide nanoparticles into chitosan polymer matrix [62]. Meanwhile, various heavy chemicals as cross-linking agents like glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether were used to achieve these [63].

5. Common Characterization of chitosan-silver nanocomposites

In most synthesis of chitosan nanocomposites, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray Diffraction (XRD) are commonly employed as analytical techniques for their characterizations [65]. This section of the review gives concise idea of these techniques.

5.1 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectroscopy is an analytical technique employed to identify mostly polymeric and organic such as chitosan nanocomposites. But, in some cases, it can also be used to analyse inorganic materials. This technique uses infrared light to observe chemical properties (functional groups) of the nanocomposites through scanning [66].

In most studies, an indication of the presence of silver nanoparticles in the polymer matrix of chitosan is the change in wave number and intensities of the characteristic bands assigned to the overlapped stretching vibrations of hydroxyl (-OH) and amino ($-NH_2$) groups of chitosan (**Figure 5**).

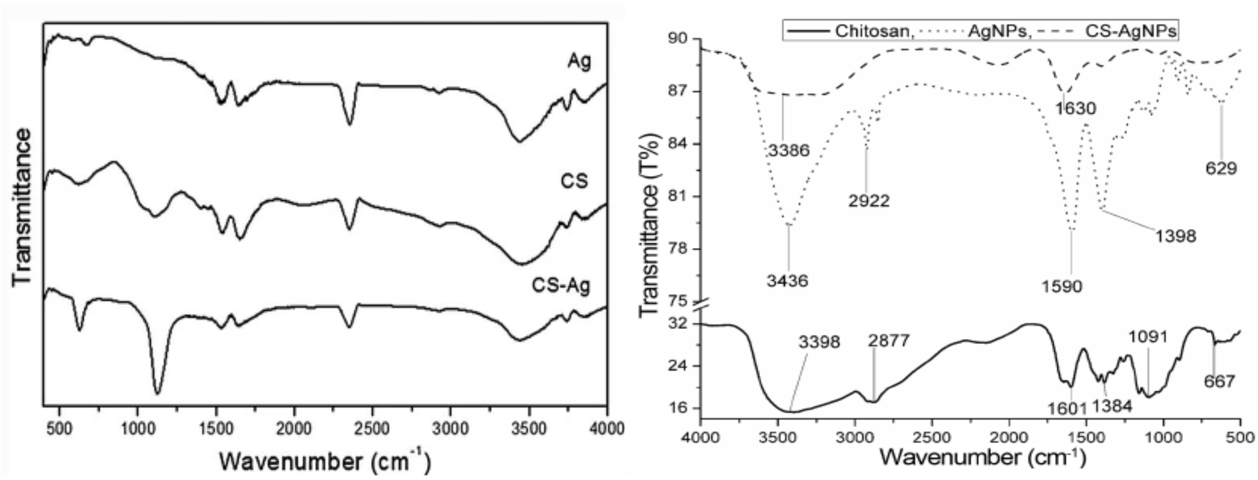

Figure 5: FTIR spectra of (a): silver nanoparticles (b): chitosan (c): chitosan-silver [67, 68].

These changes show that there is successful link between the polymer chains and the silver nanoparticles [69, 70, 71].

5.2 X-Ray Diffraction (XRD)

X-Ray Diffraction is a non-destructive analytical technique frequently employed to analyzed nanomaterials for their crystalline structures [72]. This technique helps to identify the various crystalline phases present in the material such that information regarding their chemical compositions are revealed. More so, the technique reveals the unit cell dimensions, angles of the atoms, distance of interatomic planes which are used to determine the crystallite size of the materials using Debye–Scherer formula [73]. **Figure 6** shows the X-ray diffractogram of synthesized chitosan–silver nanocomposites using different concentrations of silver nitrate as illustrated by Huang *et al.* [74]. The authors affirmed that the crystal phases of both chitosan and silver nanoparticles were indexed and also established that as the amount of silver used for preparing the nanocomposite increases the crystal phases of silver nanoparticles became more visible.

The X-ray diffractogram (**Figure 7**) of carboxymethyl chitosan–nanosilver hybrids prepared at 80 °C using different concentrations of silver nitrate were studied by [75]. They explained that the major diffraction peaks at 2θ =38.03°, 44.14°, 64.47°, 77.26°, and 81.35°in the CMC-Ag nanocomposites matched to the (111), (200), (220), (311), and (222) planes of silver crystals while the decrease in the intensities of characteristic peaks indicates decrease in the concentrations of silver in the nanocomposites.

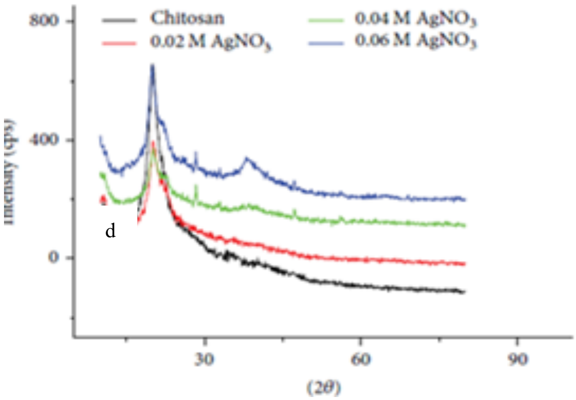

Figure 6: X-ray diffractogram of chitosan and chitosan-Ag nanocomposites prepared using 0.02M, 0.04M, and0.06M $AgNO_3$ **[76]**.

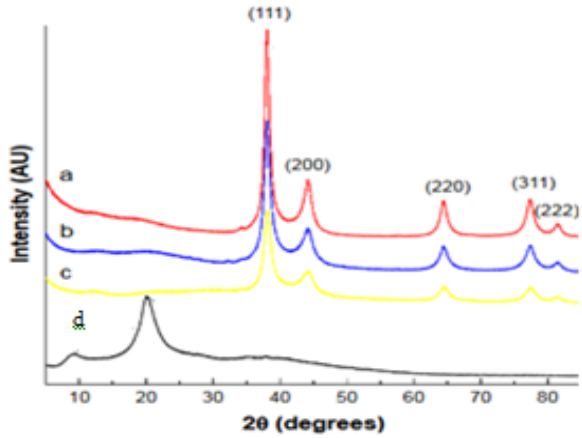

Figure 7: XRD patterns of cMc-ag1 (a), cMc-ag2 (b), cMc-ag3 (c), and cMc (d). cMc.cMc-ag, means carboxymethyl chitosan–nanosilver **[77]**.

From the outcomes of the XRD, it can be said that the silver nanoparticles due its nanosize found its way into the intermediate layer of chitosan causing the changes in the crystalline structure of chitosan **[78]**.

5.2 Scanning Electron Microscope (SEM)

SEM is an analytical technique which creates an image of nanomaterials by using a focused electron beam to scan over a surface of the material **[79]**. Details of surface morphology, orientation and compositions of material are obtain using signals from the interaction between electrons in the beam interact and the sample surface **[80]**. Several studies carried out revealed that the SEM images of chitosan-silver nanocomposites differ depending on the conditions of preparation. This difference is usually on the shape, smoothness and homogeneity of the surface **[81, 82, 83]**. But, their surfaces (**Figure 8**) are mostly porous and agglomerated. Upon the formation of nanocomposites, silver nanoparticles are enclosed by chitosan due to surface-surface interaction **[84]**.

6.0 Chitosan-silver nanocomposites for treatment of wastewater

Recently, due to continuous increase in industrial and anthropogenic activities, the release of pollutants into the environment increases **[87]**. Most of these pollutants like heavy metals are non-biodegradable and when build up in living organs above permissible limits through food chain may result to various degree of health disorderliness **[88]**. Thus, there is urgent need to control their presence in the environment particularly in water bodies. This needs to control their entry into the environment makes it essential to design efficient methods and materials to get rid of them from the wastewater **[89]**. Though, among the numerous existing methods often employed to treat water/wastewater include chemical precipitation, biological treatments, electro-deposition, evaporation, ion exchange and membrane separation **[90]**. These methods are usually faced by limitations which include ineffectiveness, high cost of operation, and generation of sludge, particularly when the amount of the toxic materials is very low **[91]**. In order to overcome these challenges mentioned, adsorption technique which has shown high effectiveness, low-cost and easy operation is commonly used, but itself has a problem of better adsorbent [92].

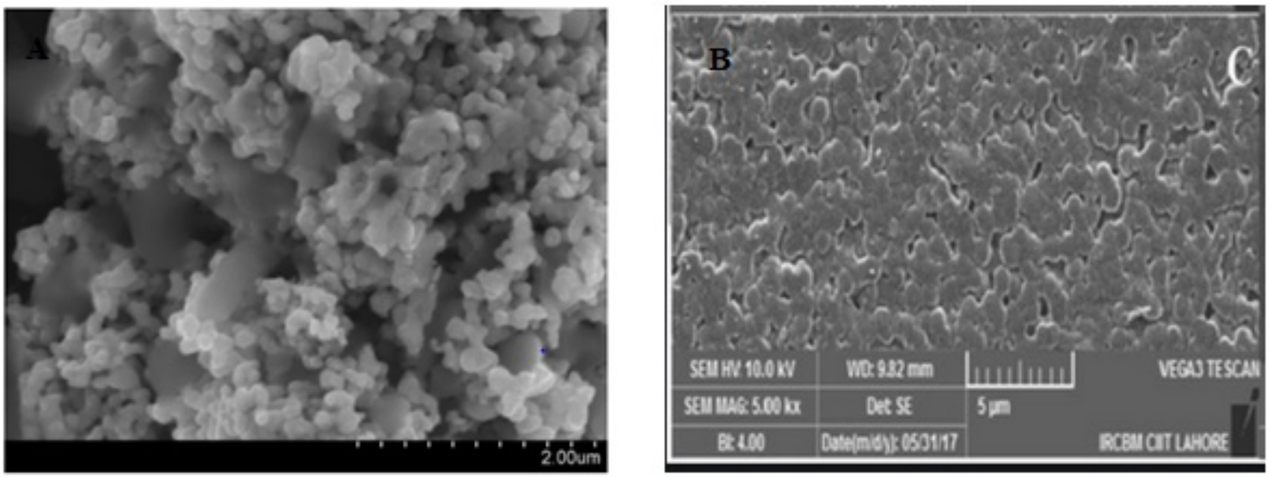

Figure 8: SEM image of chitosan-silver nanocomposite prepared by [85, 86] by In-situ chemical method using PVA/Na_2SO_4 and $NaBH_4$ as reducing agents respectively

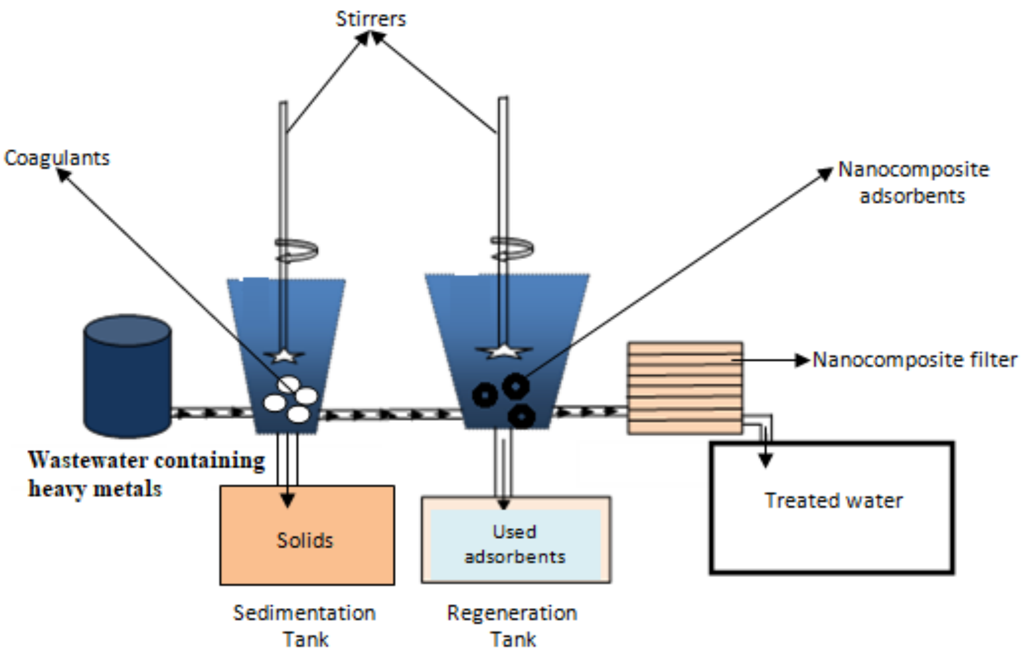

Figure 9: Application of Nanocomposite Adsorbent (*Field Study*)

Meanwhile, the existing adsorbents for toxic substance removal such as sawdust, activated carbon, zeolites and clay are faced with the problems of low adsorptive capacity, lack of large-scale implementation, non-biodegradability, unease regeneration, smaller surface area, low efficiency and effectiveness and high-cost preparation among others [93]. This calls for the search for more inexpensive adsorbents. However, biodegradable polymer such as chitosan showed to be very efficient to sequester pollutants due to their availability, low cost, presence of numerous binding sites and environmental friendliness [94]. However, as a result of its instability and low mechanical strength, its potential to remove metals from water/wastewater is limited. But, its modification through incorporation of silver nanoparticles to form nanocomposites has helped to overcome these problems [95]. This nanocomposite can be applied in the form of either adsorbent or filter (Figure 9).

Conclusion

The danger pose by heavy metal toxicity is one of the critical problems in the field of environmental science and management globally. Numerous polymer-based nanocomposites were developed for the sequestration of heavy metal ions, bacteria, virus-like microorganisms and other harmful moieties from wastewater. Among these adsorbents, biopolymers such chitosan nanocomposite is being favoured because it is inexpensive, abundant in nature and has series of functional groups as binding sites, but its dissolution using acidic media among other factors limit its application. However, incorporation of stabilizing agents like metal/metal oxide nanoparticles into the polymer network obviously enhanced its properties and hence, widen its applications. Thus, production of novel nanocomposites-based chitosan present a very remarkable approach in the area of water/wastewater treatment. Also, it was found that in most of the studies, the use of chitosan-silver nanocomposites for heavy metals removal and as well desorption experiments were not carried out. However, indicate that further studies are required in this regard

Future outlooks

In this paper, we have reviewed a series of previous studies carried out in the preparation, characterization and applications of chitosan-silver and other chitosan-based nanocomposites. Still, to better the use of chitosan nanocomposites in water pollutant remediation, further studies are required, including: choice of suitable materials to form the composites; designing for ease and eco-friendly methods to prepare the nanocomposites using the chosen materials and optimizing the preparation and adsorption parameters. Biosynthesized chitosan stabilized silver nanocomposite films that are stable and multitasking in nature should be a present research interest. From the recent available studies on chitosan nanocomposites, exceptionally well-built prospects for these nanocomposites can be foreseen, which will increase the field of use to sequestrate of heavy metals.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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